



Assessing the use of zero-valent iron microspheres to catalyze Fenton treatment processes



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ABSTRACT

The application of Fenton processes is limited by the production of iron sludge and its pH-dependence efficiency. UV-light assistance and the use of alternative catalysts as zero-valent iron (ZVI) may avoid both drawbacks favoring its potential industrial application. The use of ZVI microspheres as the catalyst of Fenton processes is herein assessed and optimized in terms of reagents dosage, particle size and surface area. Microspheres providing a surface area of 0.8 m²/g showed the best performance and the lowest tendency to be dissolved under acidic conditions, resulting a concentration ratio of [H₂O₂]/[Fe⁰] = 60 under optimal reaction conditions. The optimized 450 W UV-radiation photo-Fenton treatment addressed the almost complete mineralization of phenol (COD and TOC removal ≈ 98–99%) at both acidic and neutral initial pH values; whereas good mineralization results of oxalic acid were only achieved under acidic conditions (COD removal ≈ 100%; TOC removal ≈ 83%). Only initial neutral pH conditions enabled the recovery of the catalyst. Although a more powerful oxidation treatment was performed under acidic conditions, it also implied a higher dissolution of the microspheres. The application of less powerful radiation (100 W) limited catalyst losses under acidic conditions, but longer treatment time is required aiming to address similar degradation results.

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1. Introduction

Iron sludge generation and a better efficiency under acidic conditions limit potential applications of Fenton processes [1–2]. Therefore, new treatment configurations are necessary to minimize iron-sludge production, such as photo-assisting the process to reduce iron supply [3], and to avoid modifying the natural pH value of wastewater [4].

Particularly, the use of iron from solid sources (Fe⁰) as the catalyst has recently been successfully addressed as an interesting alternative in Fenton-like processes [5]. Iron spires, bars, powder, and even nanoscale Fe⁰ particles have already been used to catalyze the Fenton treatment of several organics [6–11] and real wastewater [12–13]. Although heterogeneous reactions have generally been addressed as much slower at equal reagents supply, they might sometimes result more efficient because they may consume

overall less H₂O₂ [5]. In addition, the main advantages of using ZVI to catalyze Fenton oxidation would be: (1) the cost saving related to using metal iron rather than iron salts, and the associated reduction of salts concentration itself in the medium; and (2) the reduction of iron-sludge generation, even completely [6].

On the other hand, the use of UV-light to assist the process is expected to improve mineralization efficiency; as it has already been addressed in other Fenton treatment configurations [3]. In fact, the degradation rate that is achieved in a photo-Fenton performance is positively enhanced when a light source is present thanks to the Fe²⁺ regeneration that is produced by Fe³⁺ reduction, the resulting generation of additional OH radicals, and the photo-decarboxylation of ferric carboxylates [3,14–17].

Finally, the performance of Fenton treatments at initial close-to-neutral pH values, which are natural in many types of wastewater even though they are far from addressing optimal results (pH = 2.8) [1], would imply a reduced addition of salts to the medium *per se*; as well as it should partially compensate treatment efficiency losses (nevertheless achieving reasonably good treatment results) along with the cost saving of avoiding the use of other chemicals to control the pH. Additionally, the application of solar radiation to heterogeneous Fenton processes may reduce its overall treatment cost.

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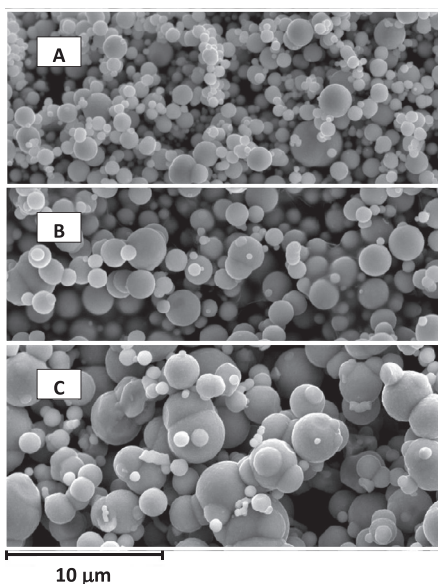


Fig. 1. SEM images of ZVI microspheres providing a catalytic surface area of 800(a), 400(b) and 200(c) m^2/kg .

The objective of this experimental research is assessing the application of ZVI microspheres as the catalyst of Fenton and photo-Fenton processes (including the alternative use of solar light) aiming to reduce catalyst use, the improvement of the separation operation and re-use of the catalyst; as well as the assessment of their application at initial neutral pH values pretending to reduce the addition of salts to the medium.

2. Material and methods

2.1. Material and analytical methods

Analytical grade chemicals were supplied by MERCK (New York, USA) and PANREAC S.A. (Barcelona, Spain). Milli Q-grade water was used to prepare solutions, all of which were stored in light-resistant Pyrex-glass bottles in the dark. Iron microspheres of different surface area, namely 200 m^2/kg (97.7% Fe), 400 m^2/kg (98.3% Fe), and 800 m^2/kg (98.3% Fe), were supplied by BASF (Ludwigshafen, Germany).

All measurements were performed according to the Standard Methods for the Examination of Water and Wastewater [18]. H_2O_2 concentration was measured by the titanium sulfate spectrophotometric method [19]. Fe^{2+} concentration by the 1,10-phenanthroline colorimetric method [20], and total soluble iron was determined under acidic conditions reducing Fe^{3+} to Fe^{2+} adding hydroxylamine.

Chemical Oxygen Demand (COD) was measured by the standardized colorimetric method at 600 nm using an Aquamate-spectrophotometer (Thermo Scientific AQA 09,1801, Waltham, USA); and Total Organic Carbon (TOC) by the combustion-infrared method with an Apollo 9000 TOC-analyzer (Tekmar Dohrmann, Ohio, USA). COD determinations were corrected considering the H_2O_2 concentration in the medium according to Hermosilla et al. [1]. pH and dissolved oxygen were measured in continuous during experiments. 2 N NaOH and 2 N H_2SO_4 solutions were used to adjust the pH of the medium.

ZVI microspheres were spectroscopically characterized (Fig. 1) using a JEOL JSM-6400 Scanning Electron Microscope coupled with an Energy Dispersive X-ray analyzer (SEM-EDX). X-ray photoelectron spectroscopy (XPS) measurements were complementarily

performed to analyze microspheres' surface in selected trials (SPECS PHOIBOS 150 MCD).

2.2. Experimental procedures

2.2.1. ZVI Fenton treatment

Phenol and oxalic acid were subjected to ZVI conventional-Fenton treatment following the same procedure. The reactor was filled with 1 l of the solution in a concentration equivalent to $\text{COD} = 475 \text{ mgO}_2/\text{l}$. The optimal H_2O_2 concentration was added in batch mode and calculated following Merayo et al. [21] as 2.148 times the value of the initial COD, which is H_2O_2 30 mM. The amount of iron microspheres to be supplied as the catalyst was calculated to test four different $[\text{H}_2\text{O}_2]/[\text{Fe}^0]$ molar ratios: 120, 60, 37.5, and 30; respectively corresponding to Fe^0 0.25, 0.5, 0.8 and 1 mM.

The solution was stirred at room temperature using a magnetic device. Two different initial pH values of the solution were tested: $\text{pH} = 2.8$ (acid), because it is the optimum value to perform Fenton treatments [1]; and $\text{pH} = 7$ (neutral) in order to assess the feasibility of not adjusting the pH before treatment. An aliquot of the solution was withdrawn from the reactor along the process at different time intervals. Half of each sample was filtered through 0.45 μm to measure H_2O_2 , Fe^{2+} , and total soluble iron contents; whereas the other half was neutralized to $\text{pH} \approx 9$ adding NaOH 2 N to stop the reaction, and then it was filtered through 0.45 μm to measure COD and TOC.

2.2.2. ZVI UV-photo-Fenton process

These trials were performed following the same procedure just described above but assisting the process with either a 450 W or a 100 W nominal power high-pressure mercury immersion UV-lamp (Models 7825-30 and 7825-34, respectively; ACE-glass, Vineland, USA). Either lamp was vertically located in the center of a quartz glass vessel reactor equipped with magnetic stirring and a cooling jacket. This whole setup was placed inside a photochemical safety cabinet (ACE-glass, Vineland, USA). Total photon fluxes of 1.1×10^{20} and 6.6×10^{18} photons/s were calculated in the photochemical reactor for the 450 W and 100 W lamps, respectively [22].

Light intensity was recorded using a radiometer (UV-VIS RM-21, UV-Elektronik, Ettlingen, Germany), resulting in 186 mW/cm^2 for the 450 W lamp, and 9.86 mW/cm^2 for the 100 W one (measured between 315 and 400 nm) 1.5 cm far from the light source at the mid-height of the UV-lamp, which was the actual distance between sample and irradiation source. The UV lamp was switched on as H_2O_2 was added to the solution (reaction time = 0).

2.2.3. ZVI solar-photo-Fenton process

These experiments were performed in a 1 l discontinuous and stirring reactor placed inside a solar simulator (Newport, Irvine, USA) equipped with a Xe-lamp of 1000 W/m^2 located in its upper part, and covered with a dark screen to prevent radiation escapes. Intensity or power can be pre-selected for each trial, and a filter is used to correct the illuminator out to obtain the solar spectrum under ideal conditions (ASTM E490-73a). The total photon flux in the photochemical reactor was 6.8×10^{19} photons/s; whereas light intensity resulted 98.9 mW/cm^2 (between 315 and 400 nm) 12 cm from the light source at the mid-surface of the Xe-lamp, which was the actual distance between sample and irradiation source. The Xe-lamp was switched on as H_2O_2 was added to the solution (reaction time = 0).

2.2.4. Oxygen-equivalent chemical-oxidation capacity (OCC)

All herein assessed ZVI-Fenton processes were compared by its oxygen-equivalent chemical-oxidation capacity (OCC), which

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